DESCRIPTION

LAMINATE

TECHNICAL FIELD
The present invention relates to a laminate.

BACKGROUND ART
The use of resin laminates is becoming the main trend in manufacturing piping materials for transferring gasoline and like fuels in view of their being processible, rustproof, lightweight and economical, among others. Because of the recent trend for regulations on fuel evaporation and emission to become more and more tightened, the demand for improvements in fuel impermeability is increasing.

So far disclosed as fuel-impermeable resin laminates are resin-made tubes resulting from lamination of a layer mainly consisting of at least one species selected from the group consisting of polybutylene terephthalate [PBT], polybutylene naphthalate [PBN], polyethylene terephthalate [PET] and polyethylene naphthalate [PEN] and a layer mainly consisting of PBT (cf. e.g. Japanese Kokai Publication 2002-213655), and resin-made tubes comprising a resin layer mainly consisting of polyphenylene sulfide [PPS] and a resin layer mainly consisting of PBT (cf. e.g. Japanese Kokai Publication 2002-267054). They have problems, however; namely, they are unsatisfactory in heat resistance, chemical resistance and solvent resistance, among others.

Fluororesins are excellent in heat resistance, chemical resistance and solvent resistance. However, fluororesins are poor in mechanical strength and dimensional stability and, in addition, expensive. It is therefore desirable that they be used in the form of laminates with another or other organic materials.

As laminates made of at least one fluororesin and at least one other organic material and showing fuel impermeability as so far proposed, there are three-layer laminates comprising a layer of polyamide 12 [PA12], a

5 layer of a tetrafluoroethylene [TFE]/perfluoro(methyl vinyl ether) [PMVE] copolymer and a layer of an ethylene/TFE copolymer [ETFE] provided with electric conductivity, or three-layer laminates comprising a layer of PA12, a layer of TFE/hexafluoropropylene copolymer [FEP] and a layer of

10 an ETFE provided with electric conductivity (cf. e.g. International Publication WO 01/18142). However, the level of fuel impermeability that has been required to be attained in recent years becomes to be higher than those three-layer copolymer laminates can attain.

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SUMMARY OF THE INVENTION

In view of the above-discussed state of the art, it is an object of the present invention to provide a laminate in which at least one fluororesin is used and which is

20 highly impermeable to fuels.

The present invention is a laminate having a layer (A) comprising a fluororesin and a layer (B) comprising a fluorine-free organic material, wherein said laminate has a fuel permeation rate of not higher than 1.5 g/m^2/day.

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DETAILED DISCLOSURE OF THE INVENTION

In the following, the invention is described in detail.

The laminate of the invention has a fuel permeation

30 rate of not higher than 1.5 g/m^2/day.

The fuel permeation rate so referred to herein is the mass of a fuel allowed to permeate per unit area per day and is the value obtained by measuring, in accordance with SAEJ 1737, the permeation at 60°C of an

35 isooctane/toluene/ethanol mixed solvent [CE10] prepared by

mixing up isooctane, toluene and ethanol in a volume ratio of 45:45:10. The laminate of the invention, which has a fuel permeation rate within the above range, can be made one having a high level of fuel impermeability. Within the above range, a lower limit to the fuel permeation rate can be 0.1 $g/m^2/day$, for instance. A preferred upper limit to the fuel permeation rate is 1.2 $g/m^2/day$, and a more preferred upper limit is 1.0 $g/m^2/day$.

The laminate of the invention is a laminate having a fluororesin layer (A) and a fluorine-free organic material layer (B).

The fluororesin is a resin comprising a fluorine-containing ethylenic polymer having a fluorine-containing ethylenic monomer-derived repeating unit. The repeating unit derived from one monomer in the polymer chain is herein sometimes referred to as "monomer unit".

The fluorine-containing ethylenic monomer so referred to herein is a fluorine- and vinyl group-containing monomer having none of the adhesive functional groups to be described later herein.

The fluorine-containing ethylenic monomer is not particularly restricted but includes, among others, tetrafluoroethylene [TFE], vinylidene fluoride [VdF], chlorotrifluoroethylene [CTFE], vinyl fluoride [VF], hexafluoroisobutene, perfluoro(alkyl vinyl ether) [PAVE] species, and a vinyl monomer represented by the general formula (I):

$$CX^3X^4=CX^1(CF_2)_nX^2 \qquad\qquad (I)$$

(wherein X^1, X^3 and X^4 are the same or different and each represents a hydrogen or fluorine atom, X^2 represents a hydrogen, fluorine or chlorine atom, and n represents an integer of 1 to 10), and one or a combination of two or more of these may be used.

The vinyl monomer represented by the above general formula (I) is not particularly restricted but includes,

among others, vinyl monomers represented by the general formula (i):

$$CH_2=CX^1(CF_2)_nX^2 \qquad\qquad (i)$$

(wherein X^1 represents a hydrogen or fluorine atom, X^2 represents a hydrogen, fluorine or chlorine atom and n represents an integer of 1 to 10), such as perfluoro(1,1,2-trihydro-1-hexene), perfluoro(1,1,5-trihydro-1-pentene); and hexafluoropropylene [HFP].

The fluorine-containing ethylenic polymer mentioned above may be one comprising not only the monomer unit derived from the above-mentioned fluorine-containing ethylenic monomer but also the monomer unit derived from a fluorine-free ethylenic monomer, if desired.

The fluorine-free ethylenic monomer so referred to herein is a vinyl group-containing monomer having no fluorine atom and none of the adhesive functional groups to be described later herein. The fluorine-free ethylenic monomer is not particularly restricted but includes, among others, ethylene [Et], propylene [Pr], 1-butene, 2-butene, vinyl chloride and vinylidene chloride, and one or a combination of two or more of these may be used.

A tetrafluoroethylene-based copolymer [TFE-based copolymer] is preferred as the above-mentioned fluorine-containing ethylenic polymer. The TFE-based copolymer so referred to herein is a polymer comprising the tetrafluoroethylene unit [TFE unit] derived from TFE. The TFE unit is represented by the molecular structure [$-CF_2-CF_2-$]. The TFE-based copolymer may be one comprising, together with the TFE-derived molecular structure, one or more of the monomer units derived from fluorine-containing ethylenic monomers other than TFE and/or the monomer units derived from fluorine-free ethylenic monomers.

The TFE-based copolymer is not particularly restricted but includes, among others, Et/TFE/HFP copolymers, Et/TFE copolymers, TFE/VdF/HFP copolymers,

TFE/PAVE copolymers, TFE/HFP copolymers, and TFE/HFP/PAVE copolymers.

The fluororesin may comprise one or a combination of two or more of the fluorine-containing ethylenic polymers.

5   The fluororesin preferably comprise a fluororesin (a) having a fuel permeation coefficient of not higher than 1 $g \cdot mm/m^2/day$.

The fluororesin (a) is preferably a perfluoro-based resin.

10   Among the fluororesins, the perfluoro-based resin is most excellent in heat resistance, chemical resistance, water repellency and oil repellency, nonstickiness, electrical insulating quality, low liquid chemical permeability and low fuel permeability, among others, and

15   the laminate having a layer of the perfluoro-based resin as a surface layer can satisfactorily manifest those features characteristic of fluororesins.

The perfluoro-based resin comprises a perfluoro-based polymer.

20   The phrase "perfluoro-based" in the above term "perfluoro-based polymer" as used herein means that the main monomer unit or units in the molecular structure of the polymer are completely fluorinated.

The main monomer unit(s) is(are) the monomer unit(s)

25   derived from one or more monomer species determining the physical properties, such as the melting point, of the polymer and generally is(are) the monomer unit(s) derived from a monomer(s) amounting to not less than 80 mole percent of the monomers from which the whole monomer units

30   in the molecular structure of the polymer are derived. The above mole fraction may be 100 mole percent, for instance.

When the above mole fraction of the main monomer unit(s) in the perfluoro-based polymer is less than 100 mole percent, the monomer unit(s) other than the main

35   monomer unit(s) may not be completely fluorinated; in this

respect, the above-mentioned perfluoro-based polymer is to be conceptually distinguished from perfluoro polymers. When the whole monomer unit(s) in the perfluoro-based polymer is the main monomer unit(s) and when the monomer unit(s) other than the main monomer unit(s) is(are) completely fluorinated, the perfluoro-based polymer, which is a perfluoro polymer, includes, within the meaning thereof, perfluoro polymers.

The perfluoro-based polymer is not particularly restricted but includes, among others, tetrafluoroethylene/perfluoro(methyl vinyl ether copolymers [MFAs] and TFE/HFP copolymers.

The above-mentioned fluororesin (a) has a fuel permeation coefficient of not higher than 1 $g \cdot mm/m^2/day$.

One or a combination of two or more of all the fluororesins can be used.

The perfluoro-based polymer to be used as the fluororesin (a) is preferably a copolymer (I) comprising the TFE unit and the perfluoro monomer unit derived from a perfluoro monomer represented by the general formula (ii):

$CF_2=CF-Rf^1$ (ii)

(wherein Rf^1 represents CF_3 or ORf^2 in which Rf^2 represents a perfluoroalkyl group containing 1 to 5 carbon atoms).

The perfluoro monomer unit may comprise one single species or two or more species.

The copolymer (I) is not particularly restricted. For example, one single species or a combination of two or more species may be used.

When two or more copolymer (I) species are used, they are well compatible with each other or one another and therefore can form layers without any distinct boundary as resulting from mixing up upon melting, and the mixing ratio is adjusted so that the layers as a whole may have a preferred fuel permeation coefficient and a preferred melting point.

When two or more copolymer (I) species are used in
forming the layer (A) in the laminate of the invention, the
copolymer (I) species employed are fed to a coextruder for
laminate manufacture without preliminary blending thereof
5   or the layers produced separately are laid one on another
and then subjected to heat melting, whereby the layer (A)
is made excellent in interlayer adhesion within the layer
(A) owing to the compatibility between or among the
copolymer species without introducing any of the adhesive
10   functional groups to be described later herein.

In cases where two or more copolymer (I) species are
used, the layer (A) in the laminate of the invention may
also be one formed following preparation of a polymer alloy
by mixing up in advance the respective copolymer (I)
15   species employed.

The copolymer (I) is not particularly restricted but
includes, among others,
(I-I) copolymers comprising 80 to 95 mole percent,
preferably 88 to 93 mole percent, of the TFE unit, and 5 to
20   20 mole percent, preferably 7 to 12 mole percent of, the
hexafluoropropylene unit,
(I-II) copolymers comprising 85 to 97 mole percent of the
TFE unit, and 3 to 15 mole percent of at least one
perfluoro monomer unit represented by the general formula
25   (iia):

$CF_2=CF-ORf^1$ (iia)

(wherein Rf^1 represents a perfluoroalkyl group containing 1
to 5 carbon atoms), and
(I-III) copolymers comprising 80 to 95 mole percent of the
30   TFE unit, and 5 to 20 mole percent in total of the
hexafluoropropylene unit and at least one perfluoro monomer
unit represented by the general formula (iia).

The monomer units described above referring to the
copolymers (I-I), (I-II) and (I-III) are main monomer units
35   in the above-mentioned perfluoro-based polymers, and the

mole percentages of the respective monomer units are the mole fractions-based on the whole amount, which is taken as 100 mole percent, of the monomers from which the main monomer units in the perfluoro-based polymers are derived.

5   The copolymers (I-III) may fall under either of the categories fluororesins (a1) and fluororesins (a2), which are to be described later herein, as a result of modification of their composition within the above range.

Among the fluororesins to be used as the fluororesin 10 (a), at least one species preferably has a fuel permeation coefficient of not higher than 0.5 $g \cdot mm/m^2/day$, more preferably not higher than 0.3 $g \cdot mm/m^2/day$.

The fluororesin (a) is preferably one comprising a fluororesin (a1) having a fuel permeation coefficient of 15 not higher than 0.3 $g \cdot mm/m^2/day$.

A preferred upper limit to the fuel permeation coefficient of the fluororesin (a1) is 0.27 $g \cdot mm/m^2/day$.

When it has the layer (A) comprising the fluororesin (a1), the laminate of the invention can readily attain such 20 a high level of fuel impermeability that the fuel permeation rate is within the above-mentioned range.

As the fluororesin (a1), there may be mentioned, for example, the copolymers (I-I) and copolymers (I-III) mentioned above.

25   The polymer constituting the fluororesin (a1) in the laminate of the invention is also preferably a chlorotrifluoroethylene copolymer [CTFE copolymer] (hereinafter sometimes referred to as "CTFE copolymer (I)") comprising CTFE, Et and/or a fluorine-containing monomer 30 since this is excellent in moldability and liquid chemical impermeability.

The "fluorine-containing monomer" so referred to herein referring to the CTFE copolymer (I) is not particularly restricted but may be any, except CTFE, of 35 those enumerated hereinabove referring to the fluorine-

containing ethylenic monomer. Preferred are, however, TFE, VdF, HFP, PAVEs or vinyl monomers represented by the general formula (i) given hereinabove. The fluorine-containing monomers may be used singly or in combination of two or more.

The CTFE copolymer (I) is not particularly restricted but includes, among others, CTFE/PAVE copolymers, CTFE/VdF copolymers, CTFE/HFP copolymers and CTFE/Et copolymers, and further includes, as at least ternary copolymers, those examples of the CTFE copolymer (II) which are to be described later herein, among others.

The polymer constituting the fluororesin (a1) may also be a chlorotrifluoroethylene copolymer (hereinafter sometimes referred to as "CTFE copolymer (II)") comprising chlorotrifluoroethylene units [CTFE units], tetrafluoroethylene units [TFE units] and monomer [A] units derived from monomers [A] copolymerizable with CTFE and TFE.

The monomer [A] is not particularly restricted but may be any, other than CTFE or TFE, of those mentioned hereinabove referring to the fluorine-containing ethylenic monomer and fluorine-free ethylenic monomer. Preferred are, however, VdF, HFP, PAVEs, or vinyl monomers represented by the general formula (i) given hereinabove.

The PAVE to be used as the monomer [A] is preferably a perfluoro(alkyl vinyl ether) represented by the general formula (ii) given hereinabove, and perfluoro(methyl vinyl ether) [PMVE] and perfluoro(propyl vinyl ether) [PPVE] are more preferred among others. From the heat resistance viewpoint, PPVE is still more preferred.

Use may be made, as the monomer [A], of one or a combination of two or more of the PAVEs and of the vinyl monomers represented by the general formula (i) given hereinabove.

The CTFE copolymer (II) is not particularly restricted but includes, among others, CTFE/TFE/HFP

copolymers, CTFE/TFE/VdF copolymers, CTFE/TFE/PAVE copolymers, CTFE/TFE/Et copolymers, CTFE/TFE/HFP/PAVE copolymers and CTFE/TFE/VdF/PAVE copolymers and, among these, CTFE/TFE/PAVE copolymers are preferred.

5   Preferably, the CTFE unit and the TFE unit in the CTFE copolymers amount to 90 to 99.9 mole percent, and the monomer [A] unit amounts to 10 to 0.1 mole percent. When the monomer [A] unit content is less than 0.1 mole percent, the moldability, environmental stress cracking resistance

10   and stress cracking resistance tend to become poor and, when it is above 10 mole percent, the liquid chemical impermeability, heat resistance and mechanical characteristics tend to become poor.

      In cases the monomer [A] is a PAVE, a more preferred

15   lower limit to the monomer [A] unit content is 0.5 mole percent, a more preferred upper limit is 7 mole percent and a still more preferred upper limit is 3 mole percent.

      The CTFE copolymer constitutes a resin.

      When the term "CTFE copolymer" is used herein without

20   adding such a symbol (I) or (II), the term includes, within the meaning thereof, both the CTFE copolymers (I) and the CTFE copolymers (II).

      The CTFE copolymer can be prepared by any of the conventional methods of polymerization, for example bulk

25   polymerization, solution polymerization, emulsion polymerization or suspension polymerization. Preferably, it is prepared by suspension polymerization, however.

      The CTFE copolymer is preferably one having a melting point [Tm] of 150°C to 300°C. A more preferred lower limit

30   is 170°C.

      The Tm is the temperature corresponding to the melting peak as measured at a temperature raising rate of 10°C/minute using a differential scanning calorimeter [DSC].

      Preferred as the CTFE copolymer is one for which the

35   temperature [Tx] required for 1% by mass of the CTFE

copolymer subjected to heating testing to be decomposed is not lower than 380°C. A more preferred lower limit is 390°C, and a still more preferred lower limit is 400°C.

The heat decomposition temperature [Tx] is the value obtained by measuring the temperature necessary for 1% by mass of the mass of the CTFE copolymer subjected to heating testing to be lost using a differential calorimetry/thermogravimetry apparatus [TG-DTA].

For the CTFE copolymer, the difference [Tx − Tm] between the melting point [Tm] and the temperature [Tx] for decomposition of 1% by mass of the CTFE copolymer is preferably not smaller than 100°C. When the difference is smaller than 100°C, the range within which molding is possible is so narrow that there is only a narrow range of choice of molding conditions. Since the above-mentioned CTFE copolymer has a broad temperature range in which molding is possible, as mentioned above, a high-melting polymer can be used as a counterpart material in carrying out coextrusion molding. A preferred lower limit to the difference [Tx − Tm] is 190°C. An upper limit to the difference [Tx − Tm] may be set at 200°C, for instance, since the range of choice of molding conditions is satisfactorily broad within the above range.

The fluororesin (a) preferably further comprises, in addition to the fluororesin (a1), a fluororesin (a2) having a fuel permeation coefficient exceeding 0.3 $g \cdot mm/m^2/day$ but not higher than 1 $g \cdot mm/m^2/day$.

That laminate of the invention which has a layer (A) comprising the fluororesin (a1) and fluororesin (a2) can be readily adjusted so that it may show a desired level of fuel impermeability. A preferred upper limit to the fuel permeation coefficient of the fluororesin (a2) is 0.9 $g \cdot mm/m^2/day$, a more preferred upper limit thereto is 0.85 $g \cdot mm/m^2/day$, and a preferred lower limit is 0.35 $g \cdot mm/m^2/day$ and a more preferred lower limit is 0.4

$g \cdot mm/m^2/day$.

As examples of the fluororesin (a2), there may be mentioned those copolymer (I-II) and copolymers (I-III) mentioned hereinabove.

5　　　The fuel permeation coefficient so referred to herein is the value calculated from the change in mass, as measured at 60°C, of a sheet prepared from the measurement target resin as placed in a fuel permeation coefficient measurement cup containing an isooctane/toluene/ethanol

10　mixed solvent prepared by mixing up isooctane, toluene and ethanol in a volume ratio of 45:45:10.

The layer (A) in the laminate of the invention may be formed using a polymer alloy comprising the fluororesin (a1) and fluororesin (a2) or by lamination of the

15　fluororesin (a1) and fluororesin (a2), as described hereinabove referring to the case of using two or more copolymer (I) species, and, in the case of lamination of the fluororesin (a1) and fluororesin (a2), both the fluororesins can attain a sufficient level of adhesion

20　owing to the compatibility therebetween without introducing any of the adhesive functional groups to be described later herein.

As regards the method of forming a polymer alloy of the fluororesin (a1) and fluororesin (a2), the fluororesin

25　(a1) and fluororesin (a2) are subjected to dry blending, if desired, and the alloy formation is carried out in the conventional manner by melt kneading. In the melt kneading, use can be made of a high-temperature kneader or screw type extruder, for instance. In the case of admixing an

30　electrically conductive material (to be described later herein), the use of a twin-screw extruder is preferred so that uniform admixing of the electrically conductive material may be attained.

In the fields of application where interlayer

35　adhesion is required between the layer (A) and the

counterpart material(s) neighboring the layer (A) in the laminate of the invention, the fluororesin is preferably an adhesive fluororesin. The counterpart material is not particularly restricted but may be, for example, a layer

5   (B) comprising a fluorine-free organic material.

In cases where the counterpart material to the layer (A) is a layer (B) comprising a fluorine-free organic material, the above-mentioned adhesive fluororesin is preferably one having adhesiveness to the layer (B).

10   As the above-mentioned adhesive fluororesin, there may be mentioned ones endowed with adhesiveness, for example owing to their having an adhesive functional group or groups and/or as a result of conversion, upon heating, of a site or sites in the molecular structure, which are

15   other than an adhesive functional group or groups, to a structure or structures manifesting adhesiveness. The fluorine-containing ethylenic copolymer so referred to herein and comprising the fluororesin (a) consisting of the copolymer (I) etc. can conceptually include such adhesive

20   fluororesins. The adhesive fluororesin is preferably one having an adhesive functional group or groups since such one is excellent in adhesiveness. The term "adhesive functional group" as used herein means a functional group capable of participating in adhesion to the counterpart

25   material or materials.

The adhesive functional group is not particularly restricted but, when the fluorine-free organic material constituting the layer (B) has a polar functional group(s), it may be any of those groups capable of reacting with the

30   polar functional group(s) or capable of intermolecularly interacting, for example in the manner of hydrogen bonding.

As the adhesive functional group, there may be mentioned, among others, the carbonyl group, carbonate group, haloformyl group, formyl group, carboxyl group,

35   carbonyloxy group [-C(=O)O-], acid anhydride group [-

C(=O)O-C(=O)-], isocyanato group, amide group [-C(=O)-NH-],
imide group [-C(=O)-NH-C(=O)-], urethane bond [-NH-C(=O)O-],
carbamoyl group [NH$_2$-C(=O)-], carbamoyloxy group [NH$_2$-
C(=O)O-], ureido group [NH$_2$-C(=O)-NH-] and oxamoyl group

5   [NH$_2$-C(=O)-C(=O)-]. From the ease of introduction and/or
high reactivity viewpoint, the carbonyl portion of a
carbonate group or a haloformyl group is preferred as the
carbonyl group mentioned above.

The carbonate group is a group comprising a linkage

10   generally represented by [-OC(=O)O-] and is represented as
an -OC(=O)O-R group (in the formula, R represents an
organic group, a group I atom, a group II atom or a group
VII atom). The organic group represented by R in the above
formula is, for example, an alkyl group containing 1 to 20

15   carbon atoms, or an ether bond-containing alkyl group
containing 2 to 20 carbon atoms and preferably is an alkyl
group containing 1 to 8 carbon atoms or an ether bond-
containing alkyl group containing 2 to 4 carbon atoms,
among others. The carbonate group is, for example, -

20   OC(=O)O-CH$_3$, -OC(=O)O-C$_3$H$_7$, -OC(=O)O-C$_8$H$_{17}$, or -OC(=O)O-
CH$_2$CH$_2$OCH$_2$CH$_3$.

The haloformyl group is represented by -COY (in which
Y represents a group VII atom) and is, for example, -COF or
-COCl.

25   The number of the adhesive functional groups is to be
appropriately selected according to the counterpart
material species to be used for lamination, the shape or
form, the purpose of the adhesion, the field of use, the
bonding strength required, the tetrafluoroethylene-based

30   copolymer species, which is to be described later herein,
and the method of adhesion, among others.

The adhesive fluororesin, when it has an adhesive
functional group(s), may be one having the adhesive
functional group(s) either at a polymer chain terminus or

35   termini or on a side chain or side chains, or one

comprising a polymer having the adhesive functional group(s) both at a polymer chain terminus or termini and on a side chain or side chains. In cases where it has an adhesive functional group(s) at a polymer chain terminus or termini, it may have the same at both polymer chain termini or only at either one of the termini. In the case of the adhesive fluororesin having an adhesive functional group(s), one comprising a polymer having the adhesive functional group(s) at a polymer terminus or termini is preferred, since such will not lower the heat resistance, mechanical characteristics or chemical resistance but is advantageous from the productivity and/or cost viewpoint.

The fluorine-containing ethylenic polymer preferably has a melting point of 130 to 280°C. From the viewpoint of the ease of coextrusion molding with the fluorine-free organic material to be described later herein, such as a polyamide resin or polyolefin resin, the fluorine-containing ethylenic polymer more preferably has a melting point of 150 to 280°C, a still more preferred lower limit is 180°C and a still more preferred upper limit is 260°C.

The above-mentioned melting point of the fluorine-containing ethylenic polymer is the temperature corresponding to the melting peak upon temperature raising at a rate of 10°C/minute using a differential scanning calorimeter [DSC].

Suited for use as the fluorine-containing ethylenic polymer is a high-melting type one having a melting point of 180 to 270°C and a melt flow rate [MFR] at 297°C of 0.1 to 100 g/10 minutes so that the fuel impermeability of the product laminate may be more increased.

A more preferred lower limit to the above melting point is 200°C, and a more preferred upper limit thereto is 260°C.

The MFR is the value obtained by measuring, using a melt indexer, the mass of the fluorine-containing ethylenic

polymer flowing out, per 10 minutes, through a nozzle with a diameter of 2 mm and a length of 8 mm under a load of 5 kg.

The method of polymerization for preparing the above-mentioned fluorine-containing ethylenic polymer is not particularly restricted but includes, for example, solution polymerization, bulk polymerization and emulsion polymerization, among others. From the industrial viewpoint, however, suspension polymerization is preferred. The suspension polymerization is preferably carried out in an aqueous medium, and a fluorine-containing medium may be added thereto. As the fluorine-containing medium, there may be mentioned, among others, hydrogen-containing chlorofluoroalkanes such as CH_3CClF_2, CH_3CCl_2F, $CF_3CF_2CCl_2H$ and CF_2ClCF_2CFHCl; hydrogen-free chlorofluoroalkanes such as $CF_2ClCFClCF_2CF_3$ and $CF_3CFClCFClCF_3$; perfluoroalkanes such as $CF_3CF_2CF_2CF_3$, $CF_3CF_2CF_2CF_2CF_3$ and $CF_3CF_2CF_2CF_2CF_2CF_3$; and perfluorocycloalkanes such as perfluorocyclobutane. Perfluoroalkanes and perfluorocycloalkanes are preferred among them.

In polymerizing the fluorine-containing ethylenic polymer, the polymerization temperature is not particularly restricted but may be 0 to 100°C. The polymerization pressure is to be appropriately selected according to the solvent species employed, the amount and vapor pressure thereof, the polymerization temperature and other polymerization conditions and, generally, it may be 0 to 9.8 MPaG.

In polymerizing the fluorine-containing ethylenic polymer, an ordinary chain transfer agent, for example a hydrocarbon such as isopentane, n-pentane, n-hexane or cyclohexane; an alcohol such as methanol or ethanol; or a halogenated hydrocarbon such as carbon tetrachloride, chloroform, methylene chloride or methyl chloride, may be used for molecular weight adjustment.

Generally used as the method of adhesive functional group introduction into polymer chain terminus or termini is the method comprising carrying out the polymerization using a polymerization initiator having, within the molecule thereof, the desired adhesive functional group(s) itself(themselves) or a functional group(s) convertible to the desired adhesive functional group(s). When the adhesive functional groups are carbonyl group-containing ones, the method comprising polymerizing the respective monomers mentioned above using a peroxydicarbonate as the polymerization initiator is preferred from the viewpoint of economy, heat resistance and/or chemical resistance, among others.

The layer (A) in the laminate of the invention may be rendered electrically conductive by further incorporating an electrically conductive material in the fluororesin mentioned above. The electrically conductive material is not particularly restricted but may be, for example, an electrically conductive simple substance powder or fiber such as a metal or carbon; an electrically conductive compound powder such as zinc oxide; and a powder surface-treated for conductivity, among others.

The electrically conductive simple substance powder or fiber is not particularly restricted but includes, among others, powders of metals such as copper and nickel; metal fibers made of iron, stainless steel, etc.; carbon black, and carbon fibers.

The powder surface-treated for conductivity is a powder obtained by subjecting a nonconductive powder, such as glass beads or titanium oxide, to surface-treatment for conductivity. The treatment for conductivity is not particularly restricted but may be, for example, metal sputtering or nonelectrolytic plating. Among the electrically conductive materials, carbon black is preferably used because of its being advantageous from the

economy and/or electrostatic charge accumulation inhibition viewpoint.

In incorporating the electrically conductive material into the fluororesin, pellets are preferably prepared in advance following melt kneading.

As for the pellet heating conditions in pellet preparation after melt kneading, the pelletization is generally carried out at a temperature not lower than the glass transition temperature of the fluororesin but lower than the melting point of the fluororesin. Generally, it is carried out preferably at 130 to 200°C for 1 to 48 hours. The preliminary pellet preparation can result in uniform dispersion of the electrically conductive material in the fluororesin in the layer (A) produced and, accordingly, in uniform provision with conductivity.

The usage of the electrically conductive material is to be appropriately selected according to the fluororesin species, the conductivity characteristics required and the molding conditions, among others. Preferably, it is 1 to 30 parts by mass per 100 parts by mass of the fluororesin. A more preferred lower limit is 5 parts by mass, and a more preferred upper limit is 20 parts by mass.

The fluororesin conductive composition resulting from incorporation of the electrically conductive material in the fluororesin preferably has a surface resistance value of 1×10^0 to 1×10^9 $\Omega \cdot$cm. A more preferred lower limit is 1×10^2 $\Omega \cdot$cm, and a more preferred upper limit is 1×10^8 $\Omega \cdot$cm.

The "surface resistance value of fluororesin conductive composition" so referred to herein is the value obtained by feeding pellets obtained by melt kneading of the electrically conductive material and fluororesin to a melt indexer, heating the pellets in the melt indexer to an arbitrary temperature within the range of 200 to 400°C and measuring the surface resistance value of the extrudate

strand obtained by extrusion using a battery-powered insulation resistance tester.

The layer (A) in the laminate of the invention may further contain, in addition to the above-mentioned

5   electrically conductive material, one or more of various additives, for example stabilizers such as heat stabilizers, reinforcing agents, fillers, ultraviolet absorbers and pigments, as incorporated therein each in an amount not defeating the object of the invention. These additives can

10 render the layer (A) improved in such characteristics as heat stability, surface hardness, wear resistance, antistatic properties and weathering resistance.

The laminate of the invention has a layer (B) comprising a fluorine-free organic material.

15   The fluorine-free organic material is an organic material containing no fluorine atoms.

The fluorine-free organic material is preferably a resin coextrudable with the fluororesin of the layer (A).

The layer (B) is not required to be excellent in fuel

20 impermeability, since the laminate of the invention comprises the above-mentioned layer (A) and, therefore, even when the layer (B) is not excellent in fuel impermeability, the laminate as a whole can acquire a high level of fuel impermeability. However, the use of a fuel-

25 impermeable resin as the fluorine-free organic material is not excluded but the use of a fuel-impermeable resin is preferred.

The fuel-impermeable resin to be used as the fluorine-free organic material is preferably a resin

30 comprising a polymer high in crystallinity, more preferably a resin comprising a polar functional group-containing polymer high in crystallinity and great in intermolecular force.

The polar functional group is a functional group

35 having polarity and capable of participating in adhesion to

the adhesive fluororesin mentioned above. The polar functional group may be the same functional group as the adhesive function group which the adhesive fluororesin has, or may be a different function group.

The polar functional group is not particularly restricted but includes, for example, those mentioned hereinabove as adhesive functional groups and, further, a cyano group, sulfide groups and a hydroxyl group, among others. Among them, the carbonyloxy, cyano, sulfide and hydroxyl groups are preferred, and the hydroxyl group is more preferred.

The fluorine-free organic material is preferably a polyamide-based resin and/or a polyolefin-based resin.

The polyamide resin comprises a polymer having, within the molecule, the amide bond [-NH-C(=O)-] as a repeating unit.

The polyamide-based resin may be the so-called nylon resin comprising a polymer in which each amide bond within the molecular is bound to an aliphatic structure(s) and/or an alicyclic structure(s), or the so-called aramid resin comprising a polymer in which each amide bond within the molecule is bound to aromatic structures.

The nylon resin is not particularly restricted but includes, among others, those comprising nylon 6, nylon 66, nylon 11, nylon 12, nylon 610, nylon 612, nylon 6/66, nylon 66/12, nylon 46, a metaxylylenediamine/adipic acid copolymer, or a like polymer. Two or more of these may be used in combination.

The aramid resin is not particularly restricted but includes, among others, polyparaphenyleneterephthalamide and polymetaphenyleneisophthalamide.

The polyamide-based resin may also be one comprising a macromolecular compound having a partial structure containing no repeating unit amide bond within the molecule as resulting from block copolymerization or graft

copolymerization. As such polyamide-based resin, there may
be mentioned the resins comprising a polyamide-based
elastomer such as a nylon 6/polyester copolymer, nylon
6/polyether copolymer, nylon 12/polyester copolymer or
5   nylon 12/polyether copolymer. These polyamide-based
elastomers are the products of block copolymerization of an
oligomeric nylon and an oligomeric polyester through ester
bonding, or by block copolymerization of an oligomeric
nylon and an oligomeric polyether via ether bonding. The
10   oligomeric polyester is, for example, polycaprolactone or
polyethylene adipate, and the oligomeric polyether is, for
example, polyethylene glycol, polypropylene glycol or
polytetramethylene glycol. Preferred as the polyamide-
based elastomer are nylon 6/polytetramethylene glycol
15   copolymers and nylon 12/polytetramethylene glycol
copolymers.

As the polyamide-based resin, which can give a
satisfactory level of mechanical strength even when
polyamide-based resin layers are thin, there may be
20   mentioned, among others, nylon 6, nylon 66, nylon 11, nylon
12, nylon 610, nylon 612, nylon 6/66, nylon 66/12, nylon
6/polyester copolymers, nylon 6/polyether copolymers, nylon
12/polyester copolymers and nylon 12/polyether copolymers,
and two or more of these may be used in combination.

25   The polyolefin-based resin is a resin having a
monomer unit(s) derived from a vinyl group-containing
monomer(s) containing no fluorine atoms. The vinyl group-
containing monomer containing no fluorine atoms is not
particularly restricted but may be, for example, any of
30   those fluorine-free ethylenic monomers mentioned
hereinabove referring to the fluororesin and, in the fields
of application where a sufficient level of interlaminar
adhesion to the counterpart material of the layer (A), for
instance, is required, it is preferably one having the
35   polar functional group(s) mentioned above.

The polyolefin-based resin is not particularly restricted but includes, among others, polyolefins such as polyethylene, polypropylene, high-density polyolefins and, further, modified polyolefins resulting from modification of the polyolefins mentioned above with maleic anhydride, for instance.

As the fluorine-free organic material, there may be mentioned those polyamide-based resins and polyolefin-based resins mentioned above and, in addition, resins comprising ethylene/vinyl alcohol copolymers, polyurethane resins, polyester resins, polyaramid resins, polyimide resins, polyamideimide resins, polyphenylene oxide resins, polyacetal resins, polycarbonate resins, acrylic resins, styrenic resins, acrylonitrile/butadiene/styrene resins [ABSs], vinyl chloride-based resins, cellulosic resins, polyetheretherketone resins [PEEKs], polysulfone resins, polyethersulfone resins [PESs], polyetherimide resins, and polyphenylene sulfide resins, among others.

In the layer (B) in the laminate of the invention, there may further be incorporated one or more of various additives, for example stabilizers such as heat stabilizers, reinforcing agents, fillers, ultraviolet absorbers and pigments, each in an amount not defeating the object of the invention. These additives can render the layer (B) improved in such characteristics as heat stability, surface hardness, wear resistance, antistatic properties and weathering resistance.

In the laminate of the invention, the layer (A) and layer (B) may each comprise one single layer or have a two-layer or further multilayer structure. In cases where the layer (B) has a two-layer or further multilayer structure, it is not always necessary for two arbitrary layers to be next to each other; thus, for example, the layer (A) may be sandwiched between the arbitrary two layers.

The laminate of the invention may also be one

comprising the layer (A) and layer (B) and, further, another layer or other layers. As the other layer, there may be mentioned, for example, a protective layer comprising an elastomer, for instance, and protecting the

5 laminate against vibration, shock, etc.

Even when it is thinner than the conventional resin laminates, the laminate of the invention can acquire a high level of fuel impermeability so that the fuel permeation rate may fall within the above-mentioned range. The

10 conventional resin laminates can indeed be improved in fuel impermeability by increasing the thickness thereof. In certain fields of use, however, thin laminates are preferred and, when thin, the conventional resin laminates cannot attain a high level of fuel impermeability.

15 The laminate of the invention can be diminished in thickness to 1 mm or less, for instance, while retaining the fuel permeation rate within the range mentioned above. The thickness of the laminate of the invention may vary depending on the intended use thereof and, when it is used

20 as a fuel tube, which is to be described later herein, the thickness is preferably 1.5 mm or less, more preferably 1.0 mm or less.

The thickness of the layer (A) is preferably 0.001 to 0.5 mm, although it depends on the intended use. A more

25 preferred lower limit is 0.003 mm, a still more preferred lower limit is 0.01 mm, and a more preferred upper limit is 0.4 mm and a still more preferred upper limit is 0.3 mm.

The thickness of the layer (B) is preferably 0.005 to 5 mm, although it depends on the intended use. A more

30 preferred lower limit is 0.01 mm.

The laminate of the invention may take any of various forms, including film forms, sheet forms, tube forms, hose forms, bottle forms and tank forms, among others. The film forms, sheet forms, tube forms and hose forms may be

35 corrugated or convoluted.

When the fluororesin and fluorine-free organic
material are coextrudable, the laminate of the invention is
generally molded by the conventional multilayer coextrusion
methods, for example by the multimanifold method or
5   feedblock method.

The laminate of the invention can be used in the
following fields of application.

Films, sheets; films for foodstuffs, sheets for
foodstuffs, films for pharmaceuticals, sheets for
10   pharmaceuticals, diaphragms for diaphragm pumps, various
packing elements, etc.

Tubes, hoses; fuel tubes or fuel hoses such as auto
fuel tubes or auto fuel hoses, solvent tubes or solvent
hoses, paint tubes or pain hoses, auto radiator hoses, air
15   conditioner hoses, brake hoses, electric wire coverings,
food/drink tubes or food/drink hoses, etc.

Bottles, containers, tanks; auto radiator tanks,
gasoline tanks, other fuel tanks, solvent tanks, paint
tanks, liquid chemical containers such as containers for
20   liquid chemicals for use in semiconductor manufacture,
food/drink tanks, etc.

Others; carburetor flange gaskets, various seals for
autos such as fuel pump O rings, various mechanical seals
such as hydraulic component seals, gears, etc.

25   Since it has a fuel permeation rate of not higher
than 2 g/m^2/day, as described hereinabove, the laminate of
the invention can be adequately used as a laminate for fuel
tube for use as a fuel tube.

In cases where the laminate of the invention is to be
30   used as a laminate for fuel tube, the layer (A) is
preferred as the innermost layer of the fuel tube. The
fuel tube innermost layer, when in contact with an
inflammable liquid such as gasoline, tends to allow static
charge accumulation. For avoiding such static charge-due
35   ignition, the layer (A) is preferably one supplemented with

an electrically conductive material.

The laminate of the invention can suitably be used in the fields of application where it comes into contact with a fuel during the use thereof, for example as a tube,

5 including a fuel tube, a hose or a tank. In this case, the part coming into contact with the fuel is preferably the layer (A). Since the fuel-contacting place is generally the inner layer, the layer (B) serves as an outer layer while the layer (A) is the inner layer. The terms "outer

10 layer" and "inner layer" are used herein only to indicate the relative positions of the layer (A) and layer (B), namely which layer is the outer layer or inner layer, in a form or shape in which the inner side and outer side are conceptually distinguishable, for example in the case of

15 tubes, hoses, tanks, etc. The laminate may also comprise a further layer(s) on the surface of the layer (B) which is opposite to the surface in contact with the layer (A) and/or a layer(s) between the layer (A) and layer (B).

The concept "intermediate layer" as employed herein

20 indicates a layer occurring between the outer layer and inner layer.

In the laminate of the invention, it is not always necessary for the boundary between two layers in contact with each other to be distinct. Thus, the laminate may

25 have a layer structure such that molecular chains of the polymers constituting the respective layers show concentration gradients by entering the respective other layers through the contacting face.

The layer constitution, which is preferred, of the

30 laminate of the invention for use as a fuel tube is not particularly restricted but includes, among others, the following:

A laminate comprising

layer 1: a layer comprising an adhesive fluororesin and

35 layer 2: a layer comprising a polyamide-based resin;

A laminate comprising

layer 1: a layer comprising an adhesive fluororesin,

layer 2: a layer comprising an adhesive fluororesin and

layer 3: a layer comprising a polyamide-based resin; and

5   A laminate comprising

layer 1: a layer comprising an adhesive fluororesin,

layer 2: a layer comprising an ethylene/vinyl alcohol

copolymer,

layer 3: a layer comprising a modified polyolefin resin and

10   layer 4: a layer comprising a high-density polyolefin resin.

The layers of the above-mentioned fuel tube laminates are subjected to lamination in the order of layer number.

BEST MODES FOR CARRYING OUT THE INVENTION

15   The following examples illustrate the present invention in further detail. These examples are, however, by no means limitative of the scope of the invention.

Synthesis Example 1: Synthesis of fluororesin F-A

A 174-L autoclave was charged with 51 L of distilled

20   water and, after thorough nitrogen substitution, was further charged with 35 kg of perfluorocyclobutane and 10.4 kg of perfluoro(methyl vinyl ether) $(CF_2=CFOCF_3)$ [PMVE], and the system inside temperature was maintained at 35°C and the rate of stirring at 200 rpm. Then,

25   tetrafluoroethylene [TFE] was fed under pressure until arrival at 0.8 MPa and, thereafter, 0.38 kg of a 50% methanol solution of di-n-propylperoxydicarbobate was fed to initiate the polymerization. To compensate for the pressure reduction in the system inside as otherwise

30   resulting from the progress of the polymerization, a gas composed of TFE and PMVE in a mole ratio of 87:13 was continuously fed to maintain the system inside pressure at 0.8 MPa and the polymerization was continued for 20 hours. After pressure release to atmospheric pressure, the

35   reaction product obtained was washed with water and dried

to give 20 kg of a powder.

This powder was pelletized under the melt kneading conditions and pellet heating conditions shown in Table 1 to give a fluororesin (F-A) in pellet form.

5   In Table 1, C1, C2, C3 and C4 indicates the four temperature measurement sites on the cylinder. The temperature measurement sites were arranged at equal pitches, from C1 which was farthest from the injection nozzle to C4 which was nearest. In Table 1, AD denotes the

10   adaptor temperature, and D the die temperature.

Table 1

	Melt kneading/extrusion conditions							Pellet heating conditions	
	C1 [°C]	C2 [°C]	C3 [°C]	C4 [°C]	AD [°C]	D [°C]	Number of screw revolutions [rpm]	Temperature [°C]	Time [hr]
Synthesis Example 1	180	260	265	265	265	265	20	150	24
Synthesis Example 2	200	280	300	300	300	300	20	150	24
Synthesis Example 3	180	265	275	275	275	275	20	150	24
Synthesis Example 4	200	280	300	300	300	300	15	150	24
Synthesis Example 5	200	265	275	275	275	275	15	150	24
Synthesis Example 6	180	260	265	265	265	265	20	150	24
Synthesis Example 7	180	260	265	265	265	265	20	150	24
Synthesis Example 8	180	260	265	265	265	265	15	150	24

Synthesis Example 2: Synthesis of fluororesin F-B

35   A 174-L autoclave was charged with 47 of distilled

water and, after thorough nitrogen substitution, was
further charged with 49 kg of hexafluoropropylene, and the
system inside temperature was maintained at 34°C and the
rate of stirring at 200 rpm. Then, TFE was fed under
5   pressure until arrival at 1.03 MPa and, thereafter, 0.58 kg
of a perfluorohexane solution containing 8% by mass of the
polymerization initiator $(H(CF_2CF_2)_3COO)_2$ was fed to
initiate the polymerization. To compensate for the
pressure reduction in the system inside as otherwise
10 resulting from the progress of the polymerization, TFE was
continuously fed to maintain the system inside pressure at
1.03 MPa. During the polymerization, feeding of 0.58 kg of
the 8% (by mass) solution of $(H(CF_2CF_2)_3COO)_2$ was repeated
at 2-hour intervals until the lapse of 6 hours from the
15 start of the polymerization and, thereafter, feeding of 0.3
kg of the same solution was repeated at 2-hour intervals.
In this manner, the polymerization was continued for 15
hours. After pressure release to atmospheric pressure, the
reaction product obtained was washed with water and dried
20 to give 18 kg of a powder.

        This powder was pelletized under the melt kneading
conditions and pellet heating conditions shown in Table 1
to give a fluororesin (F-B) in pellet form.

25 Synthesis Example 3: Synthesis of fluororesin F-C
        The powder of Synthesis Example 1 and powder of
Synthesis Example 2 (10 kg each) were dry-blended using a
Henschel mixer, and the mixture was pelletized under the
melt kneading conditions and pellet heating conditions
30 shown in Table 1 to give a fluororesin (F-C) in pellet form.

Synthesis Example 4: Preparation of fluororesin F-D
conductive composition
        Using a Henschel mixer, 91 parts by mass of the dried
35 powder of fluororesin (F-B) obtained in Synthesis Example 2

was dry-blended with 9 parts by mass of an electrically conductive material (acetylene black), and the mixture was pelletized under the melt kneading conditions and pellet heating conditions shown in Table 1 to give a fluororesin

5   (F-D) conductive composition.

A bar cut out from the strand obtained on the occasion of melt flow rate measurement had a surface resistance value of 10^5 $\Omega \cdot$cm/cm, and the inner layer of the three-layer tube of Example 2 as manufactured using this

10   fluororesin conductive composition also had a surface resistance value of 10^5 $\Omega \cdot$cm/cm.

Synthesis Example 5: Preparation of fluororesin F-E conductive composition

15   The powder of Synthesis Example 1 and powder of Synthesis Example 2 (10 kg each) were dry-blended with 2.0 kg of acetylene black as an electrically conductive material using a Henschel mixer, and the resulting mixture was pelletized under the melt kneading conditions and

20   pellet heating conditions shown in Table 1 to give a fluororesin (F-E) in pellet form.

A bar cut out from the strand obtained on the occasion of melt flow rate measurement had a surface resistance value of 10^5 $\Omega \cdot$cm/cm, and the inner layer of the

25   two-layer tube of Example 4 as manufactured using this fluororesin conductive composition also had a surface resistance value of 10^5 $\Omega \cdot$cm/cm.

Synthesis Example 6: Synthesis of fluororesin F-F

30   The polymerization procedure of Example 1 was carried out in the same manner except that PMVE was used in an amount of 13 kg and the TFE gas and PMVE gas were fed continuously in a mole ratio of 84:16. Thus was obtained 20 kg of a powder.

35   This powder was pelletized under the melt kneading

conditions and pellet heating conditions shown in Table 1
to give a fluororesin (F-F) in pellet form.

Synthesis Example 7: Synthesis of fluororesin F-G

5   A 174-L autoclave was charged with 43 L of distilled
water and, after thorough nitrogen substitution, was
further charged with 87 kg of perfluorocyclobutane and 4.3
kg of perfluoro(propyl vinyl ether) $(CF_2=CFOCF_2CF_2CF_3)$
[PPVE], and the system inside temperature was maintained at
10   35°C and the rate of stirring at 200 rpm. Then, 8.4 kg of
chlorotrifluoroethylene [CTFE] was fed and, further,
tetrafluoroethylene [TFE] was fed under pressure until
arrival at 0.67 MPa and, thereafter, 0.2 kg of a 50%
methanol solution of di-n-propylperoxydicarbobate was fed
15   to initiate the polymerization.

        To compensate for the pressure reduction in the
system inside as otherwise resulting from the progress of
the polymerization, TFE and CTFE were continuously fed, in
a mole ratio of 39:61, to maintain the system inside
20   pressure at 0.67 MPa, and the polymerization was continued
for 15 hours. After pressure release to atmospheric
pressure, the reaction product obtained was washed with
water and dried to give 11 kg of a powder.

        This powder was pelletized under the melt kneading
25   conditions and pellet heating conditions shown in Table 1
to give a fluororesin (F-G) in pellet form.

Synthesis Example 8: Preparation of fluororesin F-H
conductive composition

30   Using a Henschel mixer, 91 parts by mass of the dried
powder of fluororesin (F-G) as obtained in Synthesis
Example 7 was dry-blended with 9 parts by mass of an
electrically conductive material (acetylene black), and the
mixture was pelletized under the melt kneading conditions
35   and pellet heating conditions shown in Table 1 to give a

fluororesin (F-H) conductive composition.

A bar cut out from the strand obtained on the occasion of melt flow rate measurement had a surface resistance value of 10^5 $\Omega \cdot$cm/cm, and the inner layer of the two-layer tube of Example 7 as manufactured using this fluororesin conductive composition also had a surface resistance value of 10^5 $\Omega \cdot$cm/cm.

The fluororesins obtained in Synthesis Examples 1 to 8 were subjected to the following physical property evaluations.

(1)   Determination of the number of carbonate groups

Each fluororesin in the form of a white powder or melt-extruded pellets was compression molded at room temperature to give a film with a thickness of 50 to 200 μm. This film was subjected to infrared absorption spectrometry. Since a peak due to the carbonyl group of the carbonate group [-OC(=O)O-] appears in the wavelength region of 1810 to 1815 cm^{-1} [ν(C=O)], the absorbance of that ν(C=O) peak was measured, and the number N of carbonate groups per 10^6 main chain carbon atoms in the polymer constituting the adhesive fluororesin was calculated according to the formula (a) given below.

N = 500AW/εdf   (a)

A: Absorbance of the carbonate group [-OC(=O)O-]-derived ν(C=O) peak;

ε: Molar extinction coefficient of the carbonate group [-OC(=O)O-]-derived ν(C=O) peak; based on the data for model compounds, the value of ε was estimated at ε=170 (1·cm^{-1}·mol^{-1});

W: Average molecular weight of the monomer as calculated based on the composition of the adhesive fluororesin;

d: Density of the film (g/cm^3);

f: Thickness of the film (mm).

As for the infrared spectrometric analysis conditions, scanning was performed 40 times using Perkin-Elmer FTIR

spectrometer 1760X (product of Perkin-Elmer). The IR
spectra obtained were subjected to automatic base line
judgment using Perkin-Elmer Spectrum for Windows Ver. 1.4C,
and the absorbance of the peak at 1810 to 1815 cm^{-1} was

5   determined. The film thickness was measured using a
micrometer.

(2)   Fluororesin composition determination
The composition of each fluororesin was determined by
^{19}F NMR analysis.

10   (3)   Melting point (Tm) measurement
The melting peak was recorded at a rate of
temperature raising of 10°C/minute using a Seiko
differential scanning calorimeter [DSC], and the
temperature corresponding to the maximum value was taken as

15   the melting point (Tm).

(4)   Melt flow rate (MFR) measurement of fluororesins
Using a melt indexer (product of Toyo Seiki
Seisakusho), the mass (g) of the portion of each polymer
allowed to flow out, per unit time (10 minutes), through a

20   nozzle with a diameter of 2 mm and a length of 8 mm under a
load of 5 kg was measured at each measurement temperature.

(5)   Single layer fuel permeation coefficient
determination
The resin pellets to be used in forming each

25   layer of a tubular laminate were placed in a mold with a
diameter of 120 mm, and the mold was placed in a pressing
machine. For the fluororesin pellets of Synthesis Example
1, 3, 5 or 6, the pressing machine had been heated to
260°C; for the pellets of Synthesis Example 2 or 4, at

30   280°C; and, for the pellets of Synthesis Example 7 or 8, at
240°C. The pellets were melt pressed under a pressure of
about 2.9 MPa to give a 0.15-mm-thick sheet. The sheet
obtained was placed in a SUS316 cup for permeation
coefficient measurement having an inside diameter ø of 40

35   mm and a height of 20 mm and containing 18 ml of CE10 (fuel

prepared by mixing up a mixture of isooctane and toluene in a volume ratio of 50:50 with 10% by volume of ethanol), and the changes in mass at 60°C were measured over 1000 hours. The fuel permeation coefficient ($g \cdot mm/m^2/day$) was

5 calculated from the rate of change in mass per hour, the surface area of the sheet in contact with the liquid and the sheet thickness.

The results are shown in Table 2.

10 Table 2

	Fluorine-containing ethylenic polymer	Composition [mole ratio]	Melting point [°C]	MFR [g/10 min] (Measurement temperature)	Number of carbonate groups per 10^6 main chain	Fuel permeation coefficient [$g \cdot mm/m^2/day$]
Synthesis Example 1	Fluororesin F-A	TFE/PMVE = 87.3/12.7	225	15 (265°C)	230	0.8
Synthesis Example 2	Fluororesin F-B	TFE/HFP = 87/13	250	13 (297°C)	ND	0.25
Synthesis Example 3	Fluororesin F-C	TFE/HFP/PMVE = 87.1/6.6/6.3	235	8 (265°C)	110	0.45
Synthesis Example 4	Fluororesin F-D	TFE/HFP = 87/13	250	3.2 (297°C)	ND	0.24
Synthesis Example 5	Fluororesin F-E	TFE/HFP/PMVE = 87.1/6.6/6.3	235	4.5 (297°C)	100	0.45
Synthesis Example 6	Fluororesin F-F	TFE/PMVE = 83.7/16.3	202	22 (265°C)	226	1.2
Synthesis Example 7	Fluororesin F-G	TFE/CTFE/PPVE = 38/60.5/1.5	199	12 (275°C)	198	0.18
Synthesis Example 8	Fluororesin F-H	TFE/CTFE/PPVE = 38/60.5/1.5	199	4 (275°C)	182	0.18

30 Example 1

Using a three-material three-layer film extruding machine (product of PLABOR Co., Ltd. (Plastic Kogaku Kenkyusho)) equipped with a multimanifold T die, polyamide 12 (trademark: Vestamid X7297, product of Degussa Huls AG),

35 the fluororesin (F-A) and the fluororesin (F-B) were fed to

the three extruders to form the outer layer, intermediate layer and inner layer, respectively, and molded, under the extrusion conditions shown in Table 3, into a three-material three-layer multilayer tube with an outside

5   diameter of 8 mm and an inside diameter of 6 mm.

The multilayer tube obtained was measured for interlaminar bonding strength and fuel permeation coefficient by the following methods.

(A)   Initial bonding strength measurement

10   Test specimens with a width of 1 cm were cut out from the tubular laminate and subjected to 180° peeling testing at a rate of 25 mm/minute using a Tensilon universal testing machine. The initial bonding strength (N/cm) was determined as the mean of five maxima in the elongation-

15   tensile strength graphs.

(B)   Bonding strength measurement after fuel storage

The tubular laminate was cut into 40-cm-long pieces, each piece was equipped with a 120-ml SUS 316 reservoir tank using a Swagelock coupler, a fuel prepared by admixing

20   CM15 (mixture of isooctane and toluene in a volume ratio of 50:50) with 15% by volume of methanol was filled into the assembly and, after 1000 hours of sealing at 60°C, the bonding strength (N/cm) was measured in the same manner as mentioned above under (A) and reported as the bonding

25   strength after fuel storage.

(C)   Laminate fuel permeation rate measurement

The tubular laminate was cut into 40-cm-long pieces, each piece was equipped with a 120-ml SUS 316 reservoir tank using a Swagelock coupler, the permeation of CE10 at

30   60°C was measured according to SAEJ 1737, and the fuel permeation rate ($g/m^2/day$) was calculated from the wall thickness of the tubular laminate.

The results are shown in Table 3.

35   Example 2

Using a three-material three-layer film extruding
machine (product of PLABOR) equipped with a multimanifold T
die, polyamide 12 (trademark: Vestamid X7297, product of
Degussa Huls AG), the fluororesin (F-A) and the fluororesin

5   (F-D) conductive composition were fed to the three
extruders to form the outer layer, intermediate layer and
inner layer, respectively, and molded, under the extrusion
conditions shown in Table 3, into a three-material three-
layer multilayer tube with an outside diameter of 8 mm and

10   an inside diameter of 6 mm. The multilayer tube obtained
was evaluated in the same manner as in Example 1. The
molding conditions and evaluation results are shown in
Table 3.

15   Example 3

Using a two-material two-layer film extruding machine
(product of PLABOR) equipped with a multimanifold T die,
polyamide 12 (trademark: Vestamid X7297, product of Degussa
Huls AG) and the fluororesin (F-C) were fed to the two

20   extruders to form the outer layer and inner layer,
respectively, and molded, under the extrusion conditions
shown in Table 3, into a two-material two-layer multilayer
tube with an outside diameter of 8 mm and an inside
diameter of 6 mm. The multilayer tube obtained was

25   evaluated in the same manner as in Example 1. The molding
conditions and evaluation results are shown in Table 3.

Example 4

Using a two-material two-layer film extruding machine

30   (product of PLABOR) equipped with a multimanifold T die,
polyamide 12 (trademark: Vestamid X7297, product of Degussa
Huls AG) and the fluororesin (F-E) conductive composition
were fed to the two extruders to form the outer layer and
inner layer, respectively, and molded, under the extrusion

35   conditions shown in Table 3, into a two-material two-layer

multilayer tube with an outside diameter of 8 mm and an inside diameter of 6 mm. The multilayer tube obtained was evaluated in the same manner as in Example 1. The molding conditions and evaluation results are shown in Table 3.

5

Example 5

Using a four-material four-layer film extruding machine (product of PLABOR) equipped with a multimanifold die, the fluororesin (F-C) of Synthesis Example 3, a resin comprising an ethylene/vinyl alcohol copolymer (trademark:

10   Eval F101A, melting point 183°C, MFR 1.3 g/10 minutes, product of Kuraray Co., Ltd.), a maleic acid-modified polyethylene resin (trademark: Admer NF528, melting point 120°C, MFR 2.2 g/10 minutes, product of Mitsui Chemicals,

15   Inc.) and high-density polyethylene (trademark: Novatec HD HJ340, melting point 131°C, MFR 5.0 g/10 minutes, product of Japan Polychem Corp.) were fed to the four extruders to form the innermost layer, intermediate layer 1, intermediate layer 2 and outer layer, respectively, and

20   molded in a continuous manner, under the extrusion conditions shown in Table 3, into a four-material four-layer tube with an outside diameter of 8 mm and an inside diameter of 6 mm. The strength of the interlaminar bonding between the innermost fluororesin layer and the neighboring

25   ethylene/vinyl alcohol copolymer layer was measured. The molding conditions and evaluation results are shown in Table 3.

Example 6

30   A two-material two-layer multilayer tube was molded in the same manner as in Example 3 except that the fluororesin (F-G) was used for forming the inner layer. The molding conditions and evaluation results are shown in Table 3.

35

Example 7

A two-material two-layer multilayer tube was molded in the same manner as in Example 3 except that the fluororesin (F-H) conductive composition was used for forming the inner layer. The molding conditions and evaluation results are shown in Table 3.

Comparative Example 1

Using a two-material two-layer film extruding machine (product of PLABOR) equipped with a multimanifold T die, polyamide 12 (trademark: Vestamid X7297, product of Degussa Huls AG) and the fluororesin (F-F) were fed to the two extruders to form the outer layer and inner layer, respectively, and molded, under the extrusion conditions shown in Table 3, into a two-material two-layer multilayer tube with an outside diameter of 8 mm and an inside diameter of 6 mm. The multilayer tube obtained was evaluated in the same manner as in Example 1. The molding conditions and evaluation results are shown in Table 3.

Table 3

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1
		Three-material three-layer	Three-material three-layer	Two-material two-layer	Two-material two-layer	Four-material four-layer	Two-material two-layer	Two-material two-layer	Two-material two-layer
Inner layer	Materials	Fluororesin F-B	Fluororesin F-D conductive composition	Fluororesin F-C	Fluororesin F-E conductive composition	Fluororesin F-C	Fluororesin F-G	Fluororesin F-H conductive composition	Fluororesin F-F
	Cylinder temperature [°C]	280-310	280-320	280-290	280-300	280-290	260-280	260-285	260-270
	Adaptor temperature [°C]	300	310	290	300	290	280	285	270
Intermediate layer 1	Materials	Fluororesin F-A	Fluororesin F-A			Eval F101A			
	Cylinder temperature [°C]	280-290	280-290	-	-	160-210	-	-	-
	Adaptor temperature [°C]	290	290			210			
Intermediate layer 2	Materials					Admer NF528			
	Cylinder temperature [°C]	-	-	-	-	200-230	-	-	-
	Adaptor temperature [°C]					230			
Outer layer	Materials	PA12	PA12	PA12	PA12	Novatec HDH	PA12	PA12	PA12
	Cylinder temperature [°C]	210-245	210-245	210-245	210-245	195-235	210-245	210-245	210-245
	Adaptor temperature [°C]	245	245	245	245	235	245	245	245
Extrusion conditions	Die temperature [°C]	290	300	290	290	265	280	285	290
	Line speed [m/min]	8	6	8	8	8	8	8	8
	Water temperature [°C]	10	10	10	10	10	10	10	10
Tube outside diameter [mm]		8.03	8.02	8.01	8	8.01	8	8	8.01
Wall thickness [mm]	Inner layer	0.18	0.18	0.25	0.25	0.25	0.25	0.25	0.25
	Intermediate layer 1	0.07	0.07	-	-	0.08	-	-	-
	Intermediate layer 2	-	-	-	-	0.08	-	-	-
	Outer layer	0.75	0.75	0.75	0.75	0.59	0.75	0.75	0.75
	Total wall thickness	1	1	1	1	1	1	1	1
Initial bonding strength [N/cm]		48	47	42	41	40	46	48	47
Bonding strength after fuel storage [N/cm]		37	35	33	33	31	37	40	37
Fuel permeation rate [g/m^2/day] (solvent: CE10, temperature 60°C)		0.7	0.68	0.85	0.83	0.87	0.51	0.48	2

From Table 3, it was revealed that the laminates of Example 1 and Example 2 in which an intermediate layer of adhesive fluororesin was used between a layer of polyamide 12 and a layer of a fluororesin were higher in initial

5   bonding strength and lower in fuel permeation rate as compared with the laminates of Example 3 and Example 4 which had a two-layer structure comprising polyamide 12 and a fluororesin. It was revealed that the fuel permeation rate could be much reduced without impairing the bonding

10   strength in Example 6 and Example 7 in which a CTFE copolymer was used.

INDUSTRIAL APPLICABILITY

The laminate of the invention, which has the

15   constitution described hereinabove, can have a high level of fuel impermeability. The laminate of the invention can be adequately used in the fields of use where it has a portion coming into contact with a fuel during the use thereof, for example as tubes, including fuel tubes, hoses,

20   tanks and the like.